Germanium Silicon Alloy Anode Material Capable of Tunable Overpotential by Nanoscale Si Segregation

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Supporting Information

ABSTRACT: We developed the novel electrode that enables fine control of overpotential by exploiting surface segregation that is the enrichment of one component at the surface of binary alloy. To realize this approach, we controlled the proportion of Si with low Li diffusivity at the surface by annealing the SiGe nanowire in H₂ environment at various temperatures. The resulting SiGe nanowires annealed at 850 °C exhibited high reversible capacity (>1031 mA·h·g⁻¹), and long cycle life (400 cycles) with high capacity retention (89.0%) at 0.2 C. This superior battery performance is attributed to the remaining unlithiated part acting as support frame to prevent pulverization of anode material, which results from the fine-tuning of overpotential by controlling the degree of Si segregation.

KEYWORDS: Surface segregation, overpotential, lithium ion battery anode, GeSi nanowire, cycling stability

Group IV elements are promising anode materials to attain high energy density in lithium ion batteries (LIB). Despite the high theoretical specific capacity of these elements, their tremendous volume change during lithiation/delithiation has been a critical problem because it causes irreversible fracture of anodes.¹⁻⁴ Although low-dimensional nanostructures of Si and Ge effectively release this mechanical strain, the LIB capacity rapidly fades within a few cycles, mainly due to pulverization of the anode structure as a result of repetitive morphological change of individual nanostructures. One representative approach to overcome this problem is to construct a complex nanostructure that maintains its morphology after each cycle; one example is to make nanocomposite Si or Ge structure with the buffer layer to minimize morphological change by suppressing volume expansion. For this purpose, carbon-based materials with high mechanical and electrical properties, such as amorphous carbon⁵ and reduced graphene oxide (RGO)⁶⁻⁸ have been investigated as a buffer layer and exhibit significantly improved battery performance. However, this approach should contain a large amount (i.e., 10⁻39.5 wt %) of carbon content in the electrodes to ensure the stable cycling performance. Another example is to induce formation of internal empty space that can accommodate volume expansion in the Si or Ge. A number of nanoarchitectures, such as nanotube⁹,¹⁰ porous nanowire¹¹/ nanoparticle,¹² and mesoporous Si sponge,¹³ have been

Received: March 31, 2015
Revised: May 4, 2015

DOI: 10.1021/acs.nanolett.5b01257
Nano Lett. XXXX, XXX, XXX−XXX
employed for the robust cycling of the electrode. Morphology retention in such complex nanostructures significantly improves the cycle life of LIBs, but these nanoarchitectures entail a complex synthesis process with low throughput or reduced volumetric capacity due to reduction in the volume fraction of the active material in the anode. Therefore, a simple but powerful approach is required for the practical application of anode nanostructures.

In this sense, we propose a new strategy where the structural stability of the electrode can be dramatically improved by manipulating the atomic arrangement inside the anode material using simple thermal annealing, which is differentiated from the existing methods that focus on controlling the morphology of the nanostructure to withstand the lithiation/delithiation-induced enormous mechanical stress. Manipulation of the atomic arrangement in the nanostructure enables fine control of lithium diffusion through the electrode, resulting in leaving an

Figure 1. (a,b) Representative HRTEM images of (a) Type-U SiGe NW and (b) Type-G SiGe NW. The scale bars of (a) and (b) are 4 nm. (c,d) The depth profiles of (c) Type-U SiGe NW and (d) Type-G SiGe NW from AES, red color region in cross section of NW indicates Si-rich region and green color region indicates Ge-rich region.

Scheme 1. Schematic Illustration of a Novel SiGe Anode Structure Capable of Tunable Overpotential by Nanoscale Si Segregation

“Sluggish Li diffusion at the surface due to enrichment of Si induces the formation of an unlithiated core that functions as a support frame, resulting in the robust cycling performance of the battery.
unlithiated part functioning as a support frame to sustain the morphology of Group IV element nanostructures during lithiation/delithiation cycles. The combination of Ge and Si in a single nanowire (NW) is a good candidate system for this approach. Because Si has intrinsically low electrical conductivity and slow Li diffusivity compared to Ge, the enrichment of Si at the surface of a SiGe NW induces Li to suffer from tardy solid-state diffusion in Si; this sluggish diffusion kinetics of Li in Si increases the mass transfer resistance, thus resulting in the increase of the overpotential that is required "extra voltage" to drive a Faradaic current. Considering that significantly high overpotential generally degrades the overall performance of LIBs, the fine manipulation of overpotential within a small range is important to avoid energy loss during charge/discharge cycles and degradation of cell components of LIBs; this manipulation can be realized by adjusting the Si content atomically with slow diffusion kinetics at the surface of SiGe NW. The fine-tuned overpotential via controlling the enrichment of Si at the surface causes SiGe NW to be lithiated incompletely during the charging process, resulting in the formation of a supporting frame composed of an unlithiated part.

On the basis of this concept, we prepared SiGe NW anode materials with the high Si concentration at the surface of a NW for improving stability of nanostructure during operation of LIB, which is in sharp contrast to pulverized SiGe NW where Si is uniformly distributed (Scheme 1). Ge-dominant SiGe NWs throughout which Si is uniformly distributed (Type-U SiGe NWs) were annealed in H₂ environment to induce surface segregation of Si, and the resulting NWs (Type-G SiGe NWs) show a clear Si concentration gradient in the radial direction. An LIB with Type-G SiGe NWs as the anode shows robust cycling with capacity retention of 89.0% and reversible capacity >1031 mA·h cdg⁻¹ after 400 cycles at 0.2 C. To the best of our knowledge, improving the battery performance by precise manipulation of overpotential using tailoring atomic arrangement has not been reported.

Type-U SiGe NWs were synthesized using the vapor–liquid–solid (VLS) process at 760 °C with GeCl₄ and SiCl₄ vapors as reported previously. A representative scanning electron microscope (SEM) image shows high yield of NWs with an average diameter of about 70 nm (Figure S1a in Supporting Information). A clear lattice pattern in a high-resolution transmission electron microscope (HRTEM) image of individual NWs and a distinct diffraction pattern in the corresponding fast Fourier transform (FFT) image indicate that as-grown NWs were highly crystalline without notable structural defects (Figure 1a). A Si–Ge vibration mode at 385 cm⁻¹ in Raman spectra indicates that Ge and Si are chemically bonded to each other (Supporting Information Figure S1b); energy dispersive X-ray spectrum (EDX) (Supporting Information Figure S1a) represents that the atomic compositions of Si and Ge were 14 and 86%, respectively. The spatial distributions of Si and Ge were examined using Auger electron spectroscopy (AES) while an individual NW was continuously etched using sputtered Ar+.

Note that the Auger peaks selected for the composition analysis of Si and Ge were Si (KLL) at 1620 eV and Ge (LMM) at 1150 eV, respectively. As shown in Figure 1c, atomic concentration of Si and Ge does not show significant change as sputter time increases, implying that both elements are uniformly distributed throughout Type-U SiGe NW. To realize a model system that requires a high population of Si at the surface of NW for the control of overpotential, we exploited the surface segregation by annealing as-grown Type-U SiGe NWs in H₂ environment for 1 h at 850 °C. As shown in HRTEM (Figure 1b) and SEM

Figure 2. (a) X-ray diffraction of Type-U SiGe NWs, Type-G SiGe NWs and pure Ge powder. (b) Magnified peak of (111) plane showing that the diffraction peak of Type-G SiGe NW shifted to a lower 2θ value. Each XRD spectra is normalized to the intensity of (111) plane. (c) XRD data of SiGe NW depending on Tann. (d) Corresponding compositions of Si plotted as a function of Tann.
Enrichment of Si at the surface of NW was also confirmed by X-ray diffraction (XRD). The predominance of Si at the surface results in increased thickness of native oxide layer after thermal annealing (Figure 1a,b) because the heat of formation is much lower for SiO$_2$ ($-730.4$ kJ mol$^{-1}$ at 1000 K) than for GeO$_2$ ($-387.1$ kJ mol$^{-1}$ at 1000 K).

The driving force of surface segregation in a binary alloy is generally explained as minimization of total Gibbs free energy; in this minimization, the presence of Ge at the surface of NW is energetically favorable over that of Si because Ge has lower surface energy than Si, but this distribution is opposite to our result. Nonetheless, similar inconsistency has been reported previously: Rudkevich et al. found that surface segregation of Si preferentially occurs in Si-covered Si(001) when dosed with atomic hydrogen at high temperature,$^{22}$ and Grutzmach et al. reported that surface segregation of Ge is suppressed when SiGe grows on Ge substrate in a hydrogen environment; in both cases, surface passivation by hydrogen is responsible for the reverse distribution trend because Si–H is more stable than Ge–H. Similarly, the presence of H$_2$ during annealing of our SiGe NW is the main reason that Si and Ge rearranged to increase the population of Si near the surface.

Atomic rearrangement in SiGe NW was further characterized using X-ray diffraction (XRD). Because of the high fraction of Ge, overall XRD patterns of Type-U SiGe NWs were almost identical to those of pure Ge powder (Pn3m space group, $a = 5.6580$ Å, JCPDS card No. 04-0545) (Figure 2a). The diffraction peaks that appear only in Ge powder result from the presence of GeO$_2$. However, a closer look revealed that the diffraction peaks of Type-U SiGe NWs and Type-G SiGe NWs occur at higher 2θ value than those of Ge powder; this difference indicates that the lattice constants are smaller in the NWs than in pure Ge due to the incorporation of Si in the crystal lattices of Ge. Representatively, the XRD peak of the (111) plane appears at 27.47° in Type-U SiGe NW, which corresponds to a lattice constant of 5.6120 Å (Figure 2b). The chemical composition calculated from the lattice constant based on the result of Dismukes et al.,$^{24}$ is Ge$_{0.85}$Si$_{0.15}$, which is also corroborated by EDX result of ~14 at % Si (Supporting Information Figure S1a). As shown in Figure 2b, a non-negligible peak shift to lower 2θ was observed after thermal annealing. In the case of the (111) plane, the peak shifted from 27.47° to 27.35°, which indicates that the lattice constant of Type-G SiGe NW increased to 5.6425 Å and that the chemical composition changed to Ge$_{0.94}$Si$_{0.06}$. Evaporation of Si was negligible because it has almost zero vapor pressure in our annealing conditions,$^{19}$ so this shift in diffraction peak results from an exchange reaction between Si and Ge that caused some of the Si atoms to migrate toward the surface of the crystal lattice,$^{22}$ some migrated further to the surface and were present either as amorphous Si or SiO$_2$ due to oxidation after air exposure (shown schematically in Supporting Information Figure S5).

Such an atomic rearrangement of Si and Ge in SiGe NW can be easily controlled by changing the annealing temperature ($T_{ann}$) because surface segregation is a thermodynamic result. The diffraction peak of the (111) plane gradually shifted toward a low 2θ value as $T_{ann}$ was increased from 600 to 900 °C at a fixed annealing time of 1 h (Figure 2c). The corresponding compositions were plotted as a function of $T_{ann}$ (Figure 2d) and the plot was used as an indicator for degree of Si surface segregation. The relative fraction of Si in crystalline Ge phase of NWs did not change at $T_{ann} < 600$ °C; that is, the thermal energy was not sufficient to induce atomic rearrangement.
However, the fraction of Si started to decrease at $T_{\text{ann}} = 650 \, ^\circ\text{C}$ and reached a minimum of $\sim 6$ at $T_{\text{ann}} = 850 \, ^\circ\text{C}$. Further increase of $T_{\text{ann}}$ caused critical damage in NW morphology (Supporting Information Figure S6), but no obvious change in chemical composition. Controllable Si segregation depending on $T_{\text{ann}}$ enables manipulating overpotential for lithiation because the overpotential is determined by the proportion of Si with low Li diffusivity at the surface of NWs.

To examine Li diffusivity of SiGe NWs depending on the degree of Si segregation and corresponding overpotentials during lithiation/delithiation representative electrodes of Type-G SiGe NWs ($T_{\text{ann}} = 700, 850 \, ^\circ\text{C}$) and Type-U SiGe NWs that had different degrees of Si segregation were fabricated in Li half-cells (2016R). The values of Li diffusivity and overpotential were estimated via galvanostatic intermittent titration technique (GITT) at voltage window between 0.005 and 1.5 V at a rate of 0.1 C (120 mA·g$^{-1}$, 24 °C) (Supporting Information Figure S7), which results were plotted as a function of Li stoichiometry (Figure 3a,b). As the proportion of Si with low Li diffusivity increased at the surface (Type-U SiGe NW < Type-G SiGe NW, 700 °C < Type-G SiGe NW, 850 °C; Figure 2d), measured Li diffusivity showed a tendency to decrease as we can intuitively understand; the overpotential corresponding to each sample increased because of higher mass transfer resistance resulting from tardy solid-state diffusion of Li. The change of overpotential depending on degree of Si segregation also affects the electrochemical property during cycles (cyclic voltammogram in Supporting Information Figure S8).

On the basis of tunable overpotential, our novel electrode notably improves the structural stability during charge–discharge cycles of LIB. The Li half-cells of Type-G SiGe NWs ($T_{\text{ann}} = 700, 850 \, ^\circ\text{C}$), and Type-U SiGe NWs with different overpotential each other were tested at 1 C to compare the cycling performance (Figure 3c and Supporting Information Figure S9). Beforehand, for the formation of smooth solid electrolyte interphase (SEI), the cells were cycled at a low rate of 0.05 C during the first cycle in the voltage window between 0.005 and 1.5 V. During the initial cycles, the capacity decreased gradually as overpotential increased (Figure 3b); this trend is reasonable because it requires more energy to drive lithiation reaction as the overpotential increases. Considering the trade-off between enhanced cycle life and decreased capacity, the overall performance of Type-G SiGe NWs (850 °C) was superior to that of the Type-U and Type-G SiGe NWs (700 °C), showing reversible capacity $>1031$ mA·h·g$^{-1}$ with capacity retention of 90.0% even after 300 cycles. In contrast, when Type-G SiGe NWs (700 °C) with lower overpotential were used, although the cell showed slightly higher capacity of 60 mA·h·g$^{-1}$ than that of Type-G SiGe NWs (850 °C) during initial cycles, cycling performance is less stable showing only capacity retention of 14.7% after 300 cycles. When Type-U SiGe NWs with uniform Si distribution were used, the capacity rapidly faded after 115 cycles and declined to 10 mA·h·g$^{-1}$ after 175 cycles. Given that the rapid capacity fading of Group IV element anode is concerned with pulverization of it due to volume expansion during cycle, the robust cycling of Type-G SiGe NW (850 °C) indicates that structural stability of electrode is significantly improved. This can be also observed from ex situ TEM measurement of electrodes after 200 cycles (Supporting Information Figure S10), showing the original 1D structure of Type-G SiGe NW (850 °C) maintained whereas 1D structure of Type-U SiGe NW was obliterated during 200 cycles. It is quite remarkable that the rearrangement of Si atoms that constitute only 5 wt % of the whole NW can effectively relieve the severe deformation of the electrode structure. This superior cycling performance of Type-G SiGe NWs (850 °C) is attributed to the unlithiated

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Figure 4. (a) HRTEM image of Type-G SiGe NWs (850 °C) after the first cycle. HRTEM image of (b) the upper selected area and (c) the lower selected area of (a), showing the unlithiated part near the core clearly. (d) HRTEM image of Type-U SiGe NW after the first cycle. HRTEM image of (e) the upper selected area and (f) the lower selected area of (d). Each inset is the corresponding FFT image of the selected area with a red empty rectangle (be) or entire area (cf).

DOI: 10.1021/acs.nanolett.5b01257
remnants due to their fine-tuned overpotential at the surface, which prevents the lithiated part from pulverization (detailed explanations will be given below).

The presence of the unlithiated part in the NW is confirmed by ex situ HR-TEM measurement of Type-G SiGe NW (850 °C) after the first cycle. The unlithiated part was apparently identified near core region as shown in HRTEM images and corresponding FFT images (Figure 4a–c). The outer part of Type-G SiGe NW (850 °C) changed to the amorphous state as it underwent electrochemically driven solid-state amorphization during the cycle, whereas the core remained crystalline. This crystalline part was confirmed as unlithiated part of the NW because the lattice planes of diffraction pattern are characterized as (111), (220), and (311) of Ge, that is, this part did not react with Li due to fine-tuned overpotential (Figure 4c). In contrast, in Type-U SiGe NWs outer and core parts both changed to the amorphous state after the first cycle, confirmed by HRTEM images and the diffracted amorphous ring patterns in corresponding FFT images (Figure 4d–f). It is noted that unlithiated crystalline part of Type-G SiGe NW (850 °C) after 200 cycles is difficult to be observed in HRTEM image (Supporting Information Figure S10c). However, considering stable cycling performance during 300 cycles and uncharged rest capacity of Type-G SiGe NW (850 °C) compared to Type-U SiGe NW (Figure 3c), it is assured that the unlithiated part still remained and played an important role as a buffer layer. We thought that the whole part of NWs became amorphous during long cycles because the lithiated region is changed at every cycle. Such an amorphization of NWs makes it impossible to distinguish the amorphous unlithiated part from the amorphous lithiated part with HRTEM due to low contrast difference from low atomic number of Li. That is, the absence of the crystalline part does not indicate that all the part of NW is fully lithiated.

Figure 5. (a) Voltage profiles of Type-G SiGe NWs (850 °C) between 0.005 and 1.5 V at rate of 0.2 C. For the first cycle, the cell was cycled at 0.05 C. (b) Cycling performance of Type-G SiGe NWs (850 °C) at 0.2 C. (c) Cycling performance of Type-G SiGe NWs (850 °C) plotted as discharge capacity at 0.2, 1, 4, and 10 C. (d) Voltage profiles of Li₂MnO₃/Type-G SiGe NWs (850 °C) at charge rate of 0.5 C and discharge rate of 1 C between 2.5 and 4.3 V. (e) Cycling performance of Li₂MnO₃/Li metal and Li₂MnO₃/Type-G SiGe NWs (850 °C) at charge rate of 0.5 C and discharge rate of 1 C. Note that capacity of full-cell is expressed with regard to cathode of Li₂MnO₃.
Because of the ambiguousness between amorphous unlithiated part and amorphous lithiated part on TEM, we designed the proof of concept experiment to corroborate the role of the unlithiated part as the support frame. We compared the cycling performance of Type-G SiGe NWs (850 °C) with two clearly different fractions of the unlithiated part by controlling the charging rate (high charging rate induces the higher fraction of unlithiated part than low charging rate, which can be confirmed by difference of charge capacity) (Supporting Information Figure S11). Type-G SiGe NWs (850 °C) with a higher fraction of the unlithiated part (charge rate of 10 C/ discharge rate of 10 C) had excellent cycling performance, whereas counterparts with a lower fraction of the unlithiated part (charge rate of 0.2 C/discharge rate of 10 C) showed the rapid capacity fading with the capacity retention declining to 9.7% after 300 cycles although it showed much a higher initial capacity. Therefore, the unlithiated core part of Type-G SiGe NWs (850 °C) functions as the support frame and contributes to the superior cycling performance.

Considering that fast lithiation/delithiation induces significant mechanical stress on electrodes as the C-rate increased, we need to examine if the structural stability of our electrode can be maintained during long cycles at various C-rate. We investigated the battery performance of Type-G SiGe NWs (850 °C), which is the optimized material in our electrode system at C-rate from 0.2 to 10 C. For the cell tested at 0.2 C (Figure 5a), at the first cycle the initial charge and discharge capacity were 2140 and 1506 mA·h·g⁻¹, respectively; corresponding Coulombic efficiency (CE) was 70.5%. This irreversible capacity loss during the first cycle is attributed to either the formation of SEI layer due to side reactions with the electrolyte or decomposition of any oxide layers.26 Afterward, CE was increased to average 98.8% throughout 400 cycles. Type-G SiGe NWs (850 °C) exhibited superior cyclability with capacity retention of 89.0% at 0.2 C after 400 cycles (Figure 5b). Moreover, the electrodes maintained structural stability when the C-rate is increased from 0.2 to 10 C, which is confirmed by stable capacity retention after long cycles (Figure 5c and Supporting Information Figure S12). Each case of 0.2, 1, 4, and 10 C has the maximum capacity of 1266, 1145, 1000, and 515 mA·h·g⁻¹ and the capacity retention of 91.9, 90.0, and 84.6% at 0.2, 1, and 4 C after 300 cycles and 82.4% at 10 C after 200 cycles, respectively.

Type-G SiGe NWs (850 °C) still showed high rate capability comparable to that of Type-U SiGe NWs although slight loss of capacity occurred due to increased overpotential (Supporting Information Figure S13a). The capacity of Type-G SiGe NWs (850 °C) was ~579 mA·h·g⁻¹ at 10 C (12 A·g⁻¹), which is higher than the theoretical capacity of commercialized graphite (372 mA·h·g⁻¹). It is attributed to the high mole fraction of Ge (95 wt %), which facilitates rapid Li transport in a binary alloy lattice. Additional electrochemical characterization of Type-G SiGe NWs, Type-U SiGe NWs, and Li₂MnO₃/Li metal. Morphology of Type-G SiGe NW and Type-U SiGe NW after first cycle and 200th cycle. Rate capability of Type-G SiGe NWs (850 °C) at discharge rates from 0.2 to 100 C, fixing charge rate of 0.2 C. Morphological change of Type-G SiGe NW after annealing at 900 °C. Comparison of cycling performances of discharge capacity for Type-G SiGe NWs (850 °C) at 10 C charge/discharge rate and 0.2 C charge/10 C discharge rate. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b01257.

**ASSOCIATED CONTENT**

### Supporting Information

The characterization of Type-U SiGe NW and Type-G SiGe NW, hypothesized scheme of Si surface segregation in SiGe lattice. Additional electrochemical characterization of Type-G SiGe NW, Type-U SiGe NW, and Li₂MnO₃/Li metal. Morphology of Type-G SiGe NW and Type-U SiGe NW after first cycle and 200th cycle. Rate capability of Type-G SiGe NWs (850 °C) at discharge rates from 0.2 to 100 C, fixing charge rate of 0.2 C. Morphological change of Type-G SiGe NW after annealing at 900 °C. Comparison of cycling performances of discharge capacity for Type-G SiGe NWs (850 °C) at 10 C charge/discharge rate and 0.2 C charge/10 C discharge rate. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b01257.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by IBS-R014-G2 and NRF-2013K1A3A1A32035430. Also, finical support from the IT R&D program of MOTIE/KEIT (Development of Li-rich Cathode and Carbon-free Anode Materials for High Capacity/High Rate Lithium Secondary Batteries, 10046309) is greatly acknowledged. The authors thank to Hyun Jin Park in NINT for TEM analysis.
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